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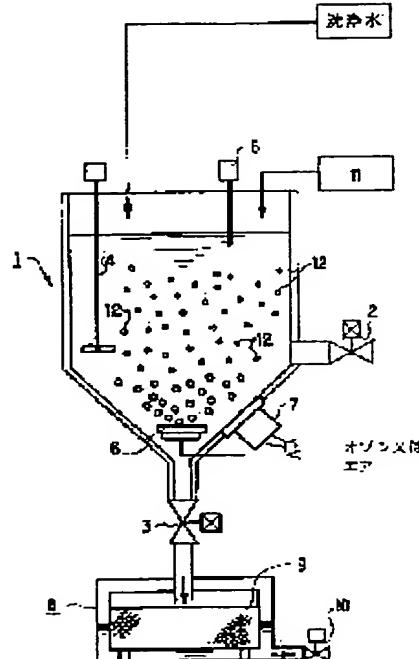
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(22)Date of filing : 27.12.1993 (72)Inventor : YAMAGATA KOJI

(54) METHOD FOR WASHING AND REGENERATING CATALYTIC FINE PARTICLES USED FOR PHOTOOXIDATION TREATMENT

(57)Abstract:

PURPOSE: To decrease the cost of a photooxidation treatment by peeling and removing sticking matters, such as a complex stuck to the surface of catalyst fine particles used in a photooxidation treating process without generating secondary pollution and repeatedly reusing expensive catalytic particles, such as titanium dioxide.

CONSTITUTION: After catalytic fine particles are suspended in water to be treated, and irradiated with ultraviolet ray to subject them organic matter decomposition or disinfecting treatment, the used catalytic fine particles 12 and washing water are added in a washing tank 1, and the catalytic fine particles 12 are washed while they are aerated by ozone or air from a diffusing plate 6. Thus, a method for washing and regenerating catalytic fine particles used for a photooxidation treating method is obtained.



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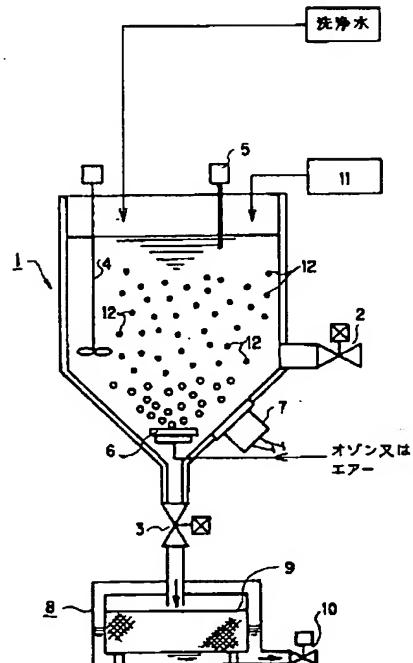
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(54)【発明の名称】光酸化処理法に使用した触媒微粒子の洗浄・再生方法

(57)【要約】

【構成】被処理水中に触媒微粒子を懸濁させ、紫外線を照射して被処理水の有機物分解乃至殺菌処理を行った後、洗浄槽1中に使用した触媒微粒子12と洗浄水を加え、散気板6からオゾン乃至エアー曝気しながら触媒微粒子12を洗浄する光酸化処理法に使用する触媒微粒子の洗浄・再生方法。

【効果】光酸化処理法に使用した触媒微粒子表面の錯体等の付着物を二次公害を起こすことなく、剥離除去することができ、また高価な二酸化チタン等の触媒粒子を繰り返して再利用できるため、光酸化処理法にコスト低減に大きな貢献をすることができる。



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【特許請求の範囲】

【請求項1】 被処理水中に触媒微粒子を懸濁させ、紫外線を照射して被処理水の有機物分解乃至殺菌処理を行った後、使用した触媒微粒子を洗浄水中でオゾン乃至エアー曝気しながら洗浄することを特徴とする光酸化処理法に使用した触媒微粒子の洗浄・再生方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 この発明は、光酸化処理法に使用した二酸化チタン等の触媒微粒子の洗浄・再生方法に関する。 10

【0002】

【従来の技術】 従来、テトロクロロエチレンなどのハログン化有機物を含む排水、塩素剤と有機物質との反応によって生成される発ガン性物質は、液体の状態で分解して無害化する方法がなく、このためこれまで高温で燃焼させて分解するとか、コンクリート中に詰めて廃棄するなどの方法が採用されていたが、何れの方法も二次公害の発生の問題がある。

【0003】 これに対して、被処理水中に二酸化チタン等の触媒微粒子を懸濁させた被処理水中に紫外線を照射させて行う光酸化処理法は、これら従来の廃水処理技術では処理できなかったテトラクロロエチレン等のハログン化有機物を含む廃水中の有機物を分解できるので、二次公害を防止する面から注目されている。 20

【0004】

【発明が解決しようとする問題点】 しかし、この方法においては使用後の酸化チタン等の触媒微粒子を処理後の水中から分離、回収が極めて困難であるという問題点があり、また使用後の触媒微粒子の再利用の問題点がある。 30

【0005】 前者の問題については、本願発明者は先に二酸化チタンを含む処理水を限外濾過膜を通過させて二酸化チタン微粒子を処理水を分離して回収する方法を提案した(特願平1-118581号)。

【0006】 しかし、この方法では限外濾過膜で捕集した触媒微粒子を処理槽に戻して何度も使用できるが、触媒微粒子を被処理水中で繰り返し使用するうちに、触媒微粒子の表面に有機物または無機物等が錯体化して固着し、或は触媒微粒子の表面が着色され、このため徐々に触媒としての機能が低下することになる。 40

【0007】 しかも、これら触媒表面に付着した錯体等は水洗等では容易に剥離せず、また一般的のアルカリ剤、酸性剤等を使用して溶解させる場合には、溶解後の廃液の処理が不完全の場合には二次公害の問題を引き起こすことになる。

【0008】 そこで、二酸化チタン等の触媒微粒子をある程度使用した後は、これを廃棄して新しい触媒に取り替えることが行われていたが、これは光酸化処理法のコストを引き上げる大きな要因となっており、この点から 50

後者の問題の完全な解決が要望されている。

【0009】

【問題点を解決するための手段】 以上の問題点を解決するため、この発明では被処理水中に触媒微粒子を懸濁させ、紫外線を照射して被処理水の有機物分解乃至殺菌処理を行った後、使用した触媒微粒子を洗浄水中でオゾン乃至エアー曝気しながら洗浄する光酸化処理法に使用する触媒微粒子の洗浄・再生方法を提案するものである。

【0010】

【作用】 即ち、この発明のように洗浄水中でオゾン乃至エアー曝気しながら触媒微粒子を洗浄すると、触媒微粒子の表面に付着した錯体等にオゾン乃至エアーの気泡が入り込み、その酸化力と浮遊力でこれら付着物を触媒微粒子の表面から剥離する。

【0011】 しかも、ここでエアー勿論のこと、オゾンについても分解して酸素となるため、全く二次公害の問題がない。

【0012】 また、以上のようなオゾン乃至エアー曝気による化学的物理的な洗浄方法に加えて、アルカリ水、酸性水による触媒微粒子の表面の化学的な洗浄方法、超音波振動による物理的な洗浄方法を行ってもよい。

【0013】 なお、化学的な洗浄方法に使用するアルカリ水、酸性水としては例えば5%の食塩水の電気分解によって生成したアルカリ水と酸性水が二次公害防止の面から好ましい。

【0014】 即ち、例えば5%食塩水の電気分解によって、約pH12のアルカリ水と約pH2.0RP(酸化還元電位)100mV以上の酸性水が得られるが、このうち酸性水には対象物の電子を奪って酸化し、自身は中性化し、残留性がない、またアルカリ水には中性化する前の酸性水と混ぜることにより、中性化して、何れも二次公害の問題を生ずることがない。

【0015】

【実施例】 以下、図示の実施例に基づいてこの発明を詳細に説明すると、図1はこの発明の洗浄工程を示すもので、1は中端部に洗浄水抜きバルブ2、下端部に触媒微粒子抜きバルブ3を有する洗浄槽であって、洗浄槽1内には攪拌機4、水位電極5が挿入され、またその底部には散気板6を盛りませ、更に洗浄槽1の側壁には超音波振動器7が取り付けられる。

【0016】 洗浄槽1の下方には水抜き槽8を位置させ、この水抜き槽8には内部にフィルター管9が収納され、更にその側部には洗浄水抜きバルブ10が設けられている。

【0017】 光酸化処理工程11から送られた使用済みの二酸化チタン等の触媒微粒子12を洗浄槽1内に供給されるが、ここで図2に基づいて光酸化処理工程11を詳細に説明すると、これに使用する光酸化処理装置は紫外線ランプ13を内蔵した処理槽14と限外濾過膜15を内蔵した分離槽16とからなり、被処理水は触媒微粒子12と共に処理

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槽14内に供給し、ここでヒータ17により加熱しながら紫外線照射を受け、これにより二酸化チタン微粒子の触媒作用により被処理水中の有機物の分解、殺菌処理等が行われる。

【0018】処理された水は、圧送ポンプ18により分離槽16に送り、限外濾過膜15を通過させることにより、触媒微粒子12は限外濾過膜15で捕集し、処理水と分離し、限外濾過膜15で捕集された触媒微粒子12は洗浄水をポンプ19により限外濾過膜15の内側に圧送することにより、限外濾過膜15より解放し、解放された触媒微粒子12はその一部は処理槽14に戻し、その一部は上述のように洗浄槽1内に供給される。

【0019】また、洗浄槽1には純水或は水道水等の洗浄水を供給し、この供給は水位電極5により洗浄槽1が所定の水位に達した時に停止する。

【0020】使用済みの触媒微粒子12と洗浄水の収容された洗浄槽1では攪拌機4で内部を攪拌し、更に超音波振動器7で振動させると共に、散気板6よりオゾン乃至エアーを供給して触媒微粒子12の表面を曝気処理しながら洗浄を行う。

【0021】全ての洗浄の終了後、バルブ3を開き、洗浄された触媒微粒子12を洗浄水と共に水抜き槽8に移し、水抜き槽8では洗浄された触媒微粒子12はフィルタ一筒9に収納され、一方洗浄水はバルブ10を開くことにより、排出され、洗浄された触媒微粒子12を処理槽14に戻して再利用することができる。

【0022】

【発明の効果】以上要するに、この発明によれば光酸化処理法に使用した触媒微粒子表面の錯体等の付着物を二

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次公害を起こすことなく、剥離除去することができる。

【0023】また、この発明によれば高価な二酸化チタン等の触媒粒子を繰り返して再利用できるため、光酸化処理法にコスト低減に大きな貢献をすることができる。

【図面の簡単な説明】

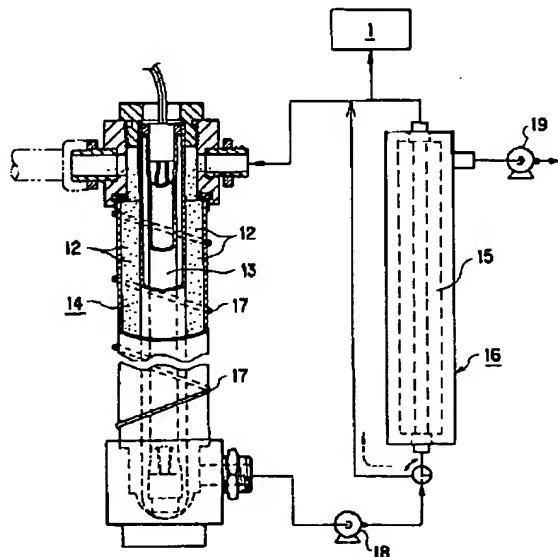
【図1】この発明の光酸化処理工程で使用した触媒微粒子の洗浄工程を示す図

【図2】触媒微粒子を使用する光酸化処理工程を示す図

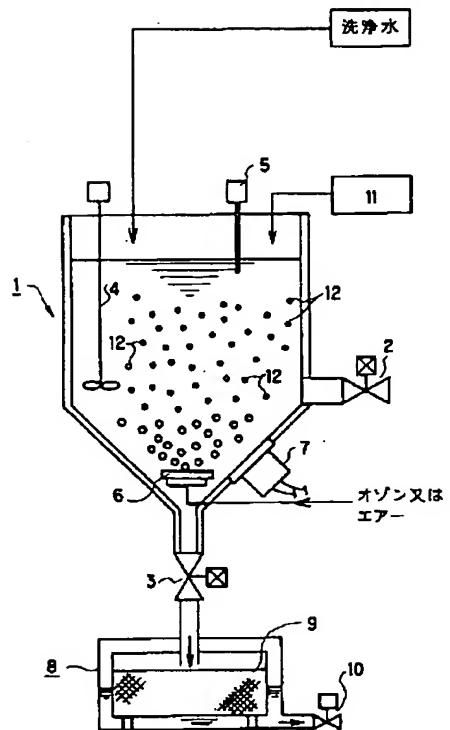
【符号の説明】

- 1は洗浄槽
- 2は洗浄水抜きバルブ
- 3は触媒微粒子抜きバルブ
- 4は攪拌機
- 5は水位電極
- 6は散気板
- 7は超音波振動器
- 8は水抜き槽
- 9はフィルタ一筒
- 10は洗浄水抜きバルブ
- 11は光酸化処理工程
- 12は二酸化チタン等の触媒微粒子
- 13は紫外線ランプ
- 14は処理槽
- 15は限外濾過膜
- 16は分離槽
- 17はヒータ
- 18は圧送ポンプ
- 19はポンプ

【図2】



【図1】



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CLAIMS

[Claim(s)]

[Claim 1] The washing / playback approach of the catalyst particle which used the used catalyst particle for the photooxidation approach characterized by ozone thru/or washing, carrying out Ayr aeration in wash water after having made processed underwater one suspend a catalyst particle, irradiating ultraviolet rays and performing organic substance decomposition thru/or sterilization processing of processed water.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention relates to the washing / playback approach of catalyst particles, such as a titanium dioxide used for the photooxidation approach.

[0002]

[Description of the Prior Art] Although the approach of wastewater containing the halogenation organic substance, such as TETORO chloroethylene, and the cancerating substance generated by the reaction of a chlorinated pesticide and an organic substance not having the approach of decomposing in the state of a liquid and defanging conventionally, making it burn at an elevated temperature until now for this reason, decomposing, or putting into concrete and discarding was adopted, any approach has the problem of generating of a secondary public nuisance.

[0003] On the other hand, since the photooxidation approach performed to the processed underwater one which made processed underwater one suspend catalyst particles, such as a titanium dioxide, by making ultraviolet rays irradiate can disassemble the organic substance in the waste water containing the halogenation organic substance, such as tetrachloroethylene which was not able to be processed with the waste-water-treatment technique of these former, it attracts attention from the field which prevents a secondary public nuisance.

[0004]

[Problem(s) to be Solved by the Invention] However, in this approach, there is a trouble that separation and recovery are very difficult, from underwater [after processing catalyst particles, such as titanium oxide after an activity,], and there is a trouble of reuse of the catalyst particle after an activity.

[0005] About the former problem, the invention-in-this-application person passed ultrafiltration membrane for the treated water which contains a titanium dioxide previously, and the approach of separating a titanium-dioxide particle and collecting treated water was proposed (Japanese Patent Application No. No. 118581 [one to]).

[0006] However, although the catalyst particle which carried out uptake by ultrafiltration membrane is returned to a processing tub and it can be used any number of times by this approach, while repeating and using a catalyst particle by processed underwater one, the organic substance or an inorganic substance will complex-ize on the front face of a catalyst particle, and it will fix on it, or the front face of a catalyst particle will be colored, and, for this reason, the function as a catalyst will fall gradually.

[0007] And in rinsing, the complex adhering to these catalyst front face etc. will cause the problem of a secondary public nuisance, when making it dissolve easily using exfoliation **** and general alkali chemicals, an acid agent, etc., and processing of the waste fluid after the dissolution is imperfection.

[0008] Then, although discarding this and exchanging for a new catalyst was performed after using catalyst particles, such as a titanium dioxide, to some extent, this is the big factor which pulls up the cost of a photooxidation approach, and perfect solution of the latter problem is demanded from this point.

[0009]

[Means for Solving the Problem] In order to solve the above trouble, by this invention, processed underwater one is made to suspend a catalyst particle, and after irradiating ultraviolet rays and performing organic substance decomposition thru/or sterilization processing of processed water, the washing / playback approach of the catalyst particle which uses the used catalyst particle for ozone thru/or the photooxidation approach washed while carrying out Ayr aeration in wash water is proposed.

[0010]

[Function] That is, ozone thru/or the air bubbles of Ayr enter into ozone thru/or the complex which adhered to the front face of a catalyst particle when the catalyst particle was washed carrying out Ayr aeration in wash water like this invention, and these affixes are exfoliated from the front face of a catalyst particle by that oxidizing power and floating force.

[0011] and here -- Ayr -- since it decomposes also about ozone and becomes oxygen of course, there is no problem of a secondary public nuisance.

[0012] Moreover, in addition to the chemical physical washing approach by the above ozone thru/or the Ayr aeration, the chemical washing approach of the front face of the catalyst particle by the alkaline water and acid water and the physical washing approach by supersonic vibration may be performed.

[0013] In addition, the alkaline water used for the chemical washing approach, the alkaline water generated by electrolysis of 5% of brine as acid water, and acid water are desirable from the field of secondary prevention of pollution.

[0014] namely, electrolysis of for example, 5% brine -- about -- about [pH 12 alkaline water and] -- pH 2 and ORP(oxidation reduction potential) 1000mV Although the above acid water is obtained, by taking the electron of an object in acid water, oxidizing, carbonating self, and not having a residual property and mixing acid water before carbonating in the alkaline water, it carbonates and neither produces the problem of a secondary public nuisance.

[0015]

[Example] Hereafter, if this invention is explained to a detail based on the example of a graphic display, by drawing 1 showing the washing process of this invention, will be the cleaning tank with which 1 has the wash water omission bulb 2 at the inside edge, and has the catalyst particle omission bulb 3 in the soffit section, and an electrode 5 will be inserted at least for an agitator 4 and water into a cleaning tank 1, and a diffusion plate 6 will be made to face that pars basilaris ossis occipitalis, and the ultrasonic vibrator 7 will be further attached in the side attachment wall of a cleaning tank 1.

[0016] The scupper tub 8 is located down the cleaning tank 1, the filter cage 9 is contained by this scupper tub 8 inside, and the wash water omission bulb 10 is further formed in that flank.

[0017] Although the catalyst particles 12, such as a used titanium dioxide sent from the photooxidation down stream processing 11, are supplied in a cleaning tank 1 If the photooxidation down stream processing 11 is explained to a detail here based on drawing 2, the photooxidation processor used for this will consist of a processing tub 14 which built in the ultraviolet ray lamp 13, and a separation tub 16 which built in ultrafiltration membrane 15. Processed water is supplied in the processing tub 14 with the catalyst particle 12, and it receives UV irradiation, heating at a heater 17 here, and, thereby, disassembly of the processed underwater organic substance, sterilization processing, etc. are performed by the catalysis of a titanium-dioxide particle.

[0018] The processed water by making the separation tub 16 pass delivery and ultrafiltration membrane 15 with the feeding pump 18 When uptake of the catalyst particle 12 is carried out by ultrafiltration membrane 15, it dissociates with treated water and the catalyst particle 12 by which uptake was carried out by ultrafiltration membrane 15 feeds wash water inside ultrafiltration membrane 15 with a pump 19 From ultrafiltration membrane 15, it releases, and the released catalyst particle 12 returns the part to the processing tub 14, and the part is supplied in a cleaning tank 1 as mentioned above.

[0019] Moreover, wash water, such as pure water or tap water, is supplied to a cleaning tank 1, and at least water suspends this supply, when a cleaning tank 1 reaches predetermined water level with an electrode 5.

[0020] In the cleaning tank 1 in which the used catalyst particle 12 and wash water were held, while agitating the interior with an agitator 4 and making it vibrate with the ultrasonic vibrator 7 further, it washes, supplying ozone thru/or Ayr and carrying out aeration processing of the front face of the catalyst particle 12 from a diffusion plate 6.

[0021] A bulb 3 is moved to an aperture after termination of all washing, the washed catalyst particle 12 is moved to the scupper tub 8 with wash water, in the scupper tub 8, the washed catalyst particle 12 can be contained by the filter cage 9, and on the other hand, wash water can return the catalyst particle 12 which was discharged by open Lycium chinense and washed in the bulb 10 to the processing tub 14, and it can be reused.

[0022]

[Effect of the Invention] In short, according to this invention, exfoliation clearance of the affixes, such as a complex of the catalyst particle front face used for the photooxidation approach, can be carried out above, without causing a secondary public nuisance.

[0023] Moreover, since catalyst particles, such as an expensive titanium dioxide, can be repeated and reused according to this invention, the big contribution to cost reduction can be carried out to a photooxidation approach.

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TECHNICAL FIELD

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PRIOR ART

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, in this approach, there is a trouble that separation and recovery are very difficult, from underwater [after processing catalyst particles, such as titanium oxide after an activity,], and there is a trouble of reuse of the catalyst particle after an activity.

[0005] About the former problem, the invention-in-this-application person passed ultrafiltration membrane for the treated water which contains a titanium dioxide previously, and the approach of separating a titanium-dioxide particle and collecting treated water was proposed (Japanese Patent Application No. No. 118581 [one to]).

[0006] However, although the catalyst particle which carried out uptake by ultrafiltration membrane is returned to a processing tub and it can be used any number of times by this approach, while repeating and using a catalyst particle by processed underwater one, the organic substance or an inorganic substance will complex-ize on the front face of a catalyst particle, and it will fix on it, or the front face of a catalyst particle will be colored, and, for this reason, the function as a catalyst will fall gradually.

[0007] And in rinsing, the complex adhering to these catalyst front face etc. will cause the problem of a secondary public nuisance, when making it dissolve easily using exfoliation **** and general alkali chemicals, an acid agent, etc., and processing of the waste fluid after the dissolution is imperfection.

[0008] Then, although discarding this and exchanging for a new catalyst was performed after using catalyst particles, such as a titanium dioxide, to some extent, this is the big factor which pulls up the cost of a photooxidation approach, and perfect solution of the latter problem is demanded from this point.

[Translation done.]

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MEANS

[Means for Solving the Problem] In order to solve the above trouble, by this invention, processed underwater ones is made to suspend a catalyst particle, and after irradiating ultraviolet rays and performing organic substance decomposition thru/or sterilization processing of processed water, the washing / playback approach of the catalyst particle which uses the used catalyst particle for ozone thru/or the photooxidation approach washed while carrying out Ayr aeration in wash water is proposed.

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OPERATION

[Function] That is, ozone thru/or the air bubbles of Ayr enter into ozone thru/or the complex which adhered to the front face of a catalyst particle when the catalyst particle was washed carrying out Ayr aeration in wash water like this invention, and these affixes are exfoliated from the front face of a catalyst particle by that oxidizing power and floating force.

[0011] and here -- Ayr -- since it decomposes also about ozone and becomes oxygen of course, there is no problem of a secondary public nuisance.

[0012] Moreover, in addition to the chemical physical washing approach by the above ozone thru/or the Ayr aeration, the chemical washing approach of the front face of the catalyst particle by the alkaline water and acid water and the physical washing approach by supersonic vibration may be performed.

[0013] In addition, the alkaline water used for the chemical washing approach, the alkaline water generated by electrolysis of 5% of brine as acid water, and acid water are desirable from the field of secondary prevention of pollution.

[0014] namely, electrolysis of for example, 5% brine -- about -- about [pH 12 alkaline water and] -- pH 2 and ORP(oxidation reduction potential) 1000mV Although the above acid water is obtained, by taking the electron of an object in acid water, oxidizing, carbonating self, and not having a residual property and mixing acid water before carbonating in the alkaline water, it carbonates and neither produces the problem of a secondary public nuisance.

[Translation done.]

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EXAMPLE

[Example] Hereafter, if this invention is explained to a detail based on the example of a graphic display, by drawing 1 showing the washing process of this invention, will be the cleaning tank with which 1 has the wash water omission bulb 2 at the inside edge, and has the catalyst particle omission bulb 3 in the soffit section, and an electrode 5 will be inserted at least for an agitator 4 and water into a cleaning tank 1, and a diffusion plate 6 will be made to face that pars basilaris ossis occipitalis, and the ultrasonic vibrator 7 will be further attached in the side attachment wall of a cleaning tank 1.

[0016] The scupper tub 8 is located down the cleaning tank 1, the filter cage 9 is contained by this scupper tub 8 inside, and the wash water omission bulb 10 is further formed in that flank.

[0017] Although the catalyst particles 12, such as a used titanium dioxide sent from the photooxidation down stream processing 11, are supplied in a cleaning tank 1 If the photooxidation down stream processing 11 is explained to a detail here based on drawing 2, the photooxidation processor used for this will consist of a processing tub 14 which built in the ultraviolet ray lamp 13, and a separation tub 16 which built in ultrafiltration membrane 15. Processed water is supplied in the processing tub 14 with the catalyst particle 12, and it receives UV irradiation, heating at a heater 17 here, and, thereby, disassembly of the processed underwater organic substance, sterilization processing, etc. are performed by the catalysis of a titanium-dioxide particle.

[0018] The processed water by making the separation tub 16 pass delivery and ultrafiltration membrane 15 with the feeding pump 18 When uptake of the catalyst particle 12 is carried out by ultrafiltration membrane 15, it dissociates with treated water and the catalyst particle 12 by which uptake was carried out by ultrafiltration membrane 15 feeds wash water inside ultrafiltration membrane 15 with a pump 19 From ultrafiltration membrane 15, it releases, and the released catalyst particle 12 returns the part to the processing tub 14, and the part is supplied in a cleaning tank 1 as mentioned above.

[0019] Moreover, wash water, such as pure water or tap water, is supplied to a cleaning tank 1, and at least water suspends this supply, when a cleaning tank 1 reaches predetermined water level with an electrode 5.

[0020] In the cleaning tank 1 in which the used catalyst particle 12 and wash water were held, while agitating the interior with an agitator 4 and making it vibrate with the ultrasonic vibrator 7 further, it washes, supplying ozone thru/or Ayr and carrying out aeration processing of the front face of the catalyst particle 12 from a diffusion plate 6.

[0021] A bulb 3 is moved to an aperture after termination of all washing, the washed catalyst particle 12 is moved to the scupper tub 8 with wash water, in the scupper tub 8, the washed catalyst particle 12 can be contained by the filter cage 9, and on the other hand, wash water can return the catalyst particle 12 which was discharged by open Lycium chinense and washed in the bulb 10 to the processing tub 14, and it can be reused.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing showing the washing process of the catalyst particle used by photooxidation down stream processing of this invention

[Drawing 2] Drawing showing photooxidation down stream processing which uses a catalyst particle

[Description of Notations]

1 is a cleaning tank.

2 is a wash water omission bulb.

3 is a catalyst particle omission bulb.

4 is an agitator.

At least for water, 5 is an electrode.

6 is a diffusion plate.

7 is an ultrasonic vibrator.

8 is a scupper tub.

9 is a filter cage.

10 is a wash water omission bulb.

11 is photooxidation down stream processing.

12 is catalyst particles, such as a titanium dioxide.

13 is an ultraviolet ray lamp.

14 is a processing tub.

15 is ultrafiltration membrane.

16 is a separation tub.

17 is a heater.

18 is a feeding pump.

19 is a pump.

[Translation done.]

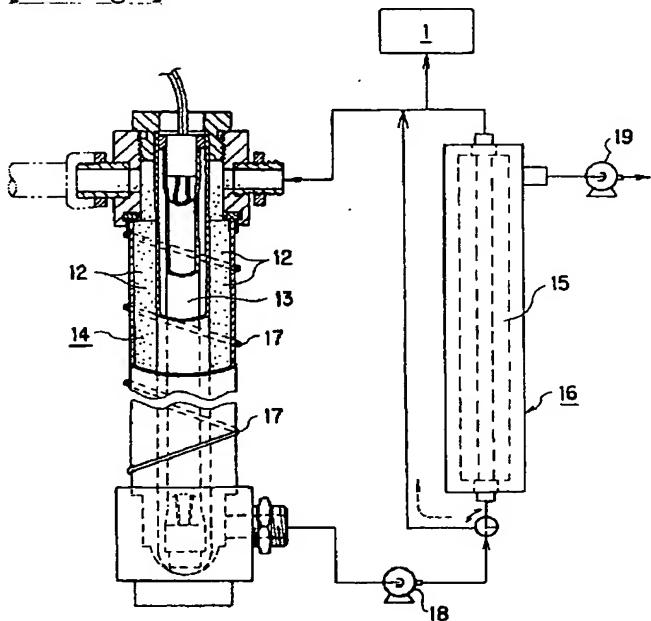
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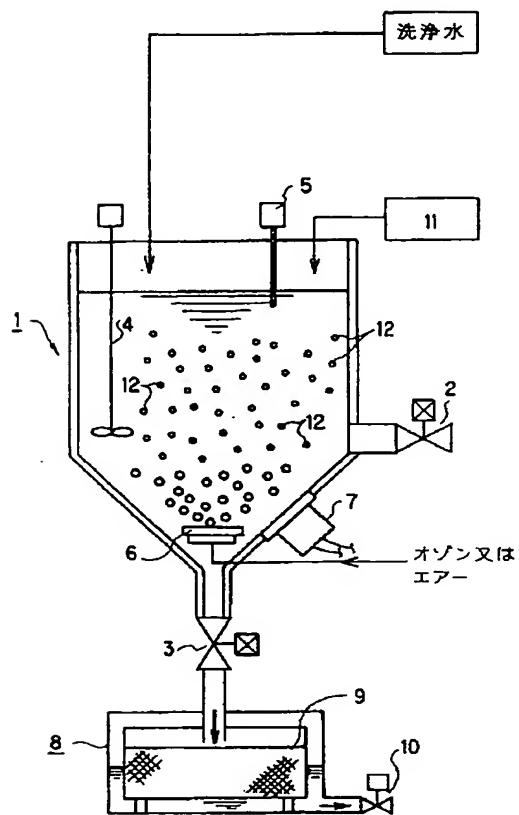
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DRAWINGS

[Drawing 2]



[Drawing 1]



[Translation done.]